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MODERN APPLIED TECHNOLOGIES FOR PRIMARY LEAD SMELTING AT THE BEGINNING OF THE 21ST CENTURY

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Abstract

During the decade of the nineties the conventional method of primary lead smelting (sinter machine/blast furnace) was successfully challenged by the introduction of novel direct and continuous smelting processes. In combination with a significant shift in market structure, as well as more stringent government regulations these modern technological innovations like the QSL, Kivcet, and Isa/Ausmelt processes became more than major competitors. They have proven to be economically and environmentally viable. The intensification of the metallurgical reaction by applying oxygen enriched or pure oxygen bath or flash smelting principles resulted in cost savings and a higher flexibility with respect to raw materials and additives usage. By synchronizing individual auxiliary plant sections with the smelting process a virtually waste-free production and low-emission mode of operation with nearly optimum energy exploitation is achieved. The primary lead industry will gradually substitute the sinter – blast furnace operation with novel high-energy efficient technologies in the new millennium.

Introduction

Despite the significantly changing patterns in the individual segments of both supply and demand for lead during the last decade, the consumption of lead has grown steadily in most countries and regions, and has well exceeded 6 million tonnes yearly worldwide (1). About 71% of all lead produced is consumed in the manufacturing of electric batteries and close to 85% of all products are recyclable. One direct consequence is the continuously rising recycling rate of lead-bearing scrap. With that high recycling rate, it is likely that most, if not all, growth in lead demand can be met without an overall increase in mine production. The combination of environmental concerns, the actual trend of decreasing net lead mine output, and an increase in smelter capacity as a result of developments in China, meant that many smelters have been forced to alter their feed mix to include a greater share of secondary materials. Today, only 80% of the lead produced by primary smelters is from lead and/or bulk concentrates, down from 88% a decade ago (2). In 2001, globally only 42% of refined lead was generated from mine production. This is much more evident in industrialized countries where only 35% of refined lead is from primary sources. More than 75% of the installed capacity is still producing lead using Dwight-Lloyd sinter machine and blast furnace operations, which was introduced at the beginning of the last century. This old practice experiences more and more difficulties being compatible with today's requirements in respect to efficiency and environmental protection. Therefore, extensive research studies have been performed in different parts of the world since the beginning of the seventies of the last century, resulting in the development of several new technologies for primary lead smelting. Most of these processes were based on direct and mainly continuous smelting technologies but only some, like the Kivcet, QSL, Isa/Ausmelt and Kaldo processes, have been realized on an industrial scale. The commercial implementation of these novel technologies towards the end of the 20th century successfully challenged the conventional method of lead smelting and most of them have proven to be economically and environmentally viable. The intensification of the metallurgical reaction by applying the bath or flash smelting principle in conjunction with the usage of oxygen resulted in cost savings and a higher flexibility with respect to raw materials and additives usage. By synchronizing individual auxiliary plant sections with the smelting process a virtually waste-free production and low-emission mode of operation with optimum energy exploitation is achieved. The primary lead industry is at a crossroad where these novel high-energy efficient technologies will gradually substitute the sinter machine – blast furnace operation. Descriptions of these technologies together with current operating results are presented in this paper.

Modern Applied Technologies

KIVCET Smelting Technology

The technology of the Kivcet process employs the principles of simultaneous flash smelting of lead bearing materials using technically pure oxygen. In conjunction with electrical energy carbon reduces the lead oxide in the slag. The process has been developed by Vniitsvetmet in Ust Kamenogorsk / Kazachstan and transferred into industrial scale after achieving satisfying operating results in the pilot plant at the Vniitsvetmet research facility.

Today, two smelters are operating based on the Kivcet technology. The first commercial scale smelter was constructed for Enirisorse at Portovesme, Sardinia. The smelter was commissioned in 1987 and its current annual production capacity is 100,000 tpy lead predominantly based on treating materials from primary sources. The second smelter was built at TeckCominco Metals in Trail, Canada and started-up in 1997. The annual capacity of the Trail smelter is up to 120,000 tpy lead. In order to meet the needs of Trail Operations as an integrated zinc-lead smelter, the smelter is designed to treat a high residue charge. Metal and co-product recoveries are maximized along with objectives of reduced energy and labor costs and reduced environmental impact.

The furnace at TeckCominco represents a more recent construction taking into consideration the operating experience at the Portovesme facility and integrating several improvements to the design. Therefore, the following technological description of the Kivcet technology and its operation is mainly focused on the smelter installed at TeckCominco. A simplified flow sheet of TeckCominco's smelter is shown in Figure 1.

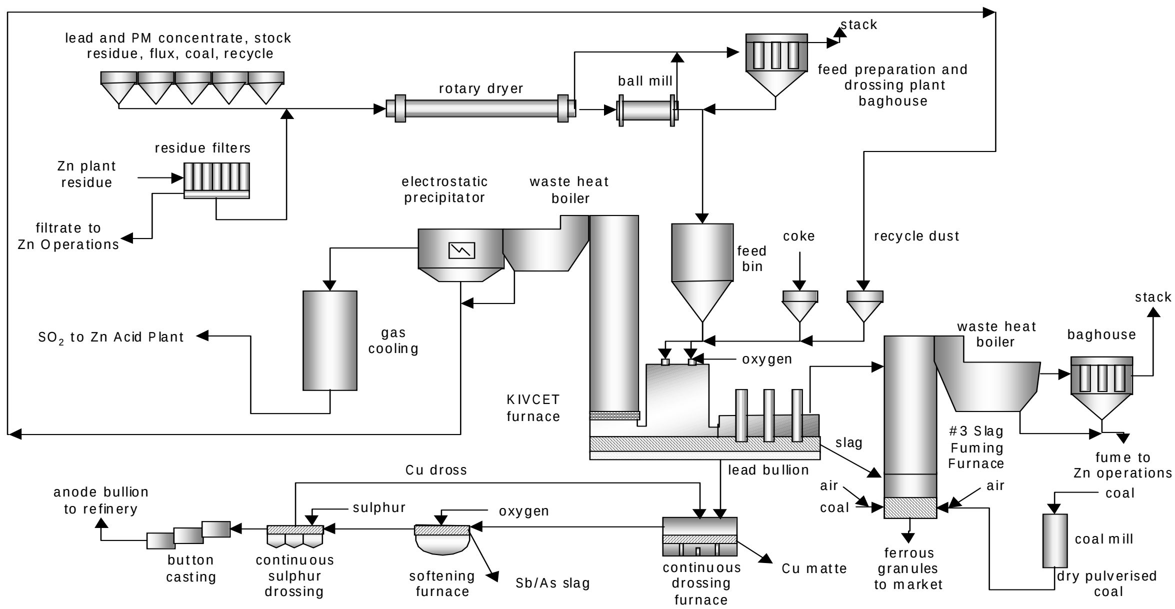

Figure 1 – Flow sheet of TeckCominco's lead smelter

The Kivcet process is able to treat a wide variety of lead bearing raw material. At the Portovesme plant the treated ratio of primary to secondary materials is about 3.5:1, while 1:2 at TeckCominco. The majority of TeckCominco's raw material consumption consists of internally generated zinc plant iron residues plus lead concentrates, precious metal concentrates as well as battery scrap. The flash smelting process requires drying of the feed material to less than 1% moisture content, prior to being charged into the furnace. The exiting dry product is conveyed from the drying furnace into a ball mill grinding it to minus 1 mm. Installed airlocks minimize the actual dried feed from fluidizing in the feed preparation system. An additionally installed vibrating screen removes coarse components originating mainly from battery scrap (grids, poles, entrained plastics etc.) to prevent a possible damage of the required airlocks (3).

The Kivcet furnace mainly consists of three primary areas, a smelting shaft, an adjoining electric furnace that is separated by a water-cooled partition wall, and the uptake shaft (Figure 2).

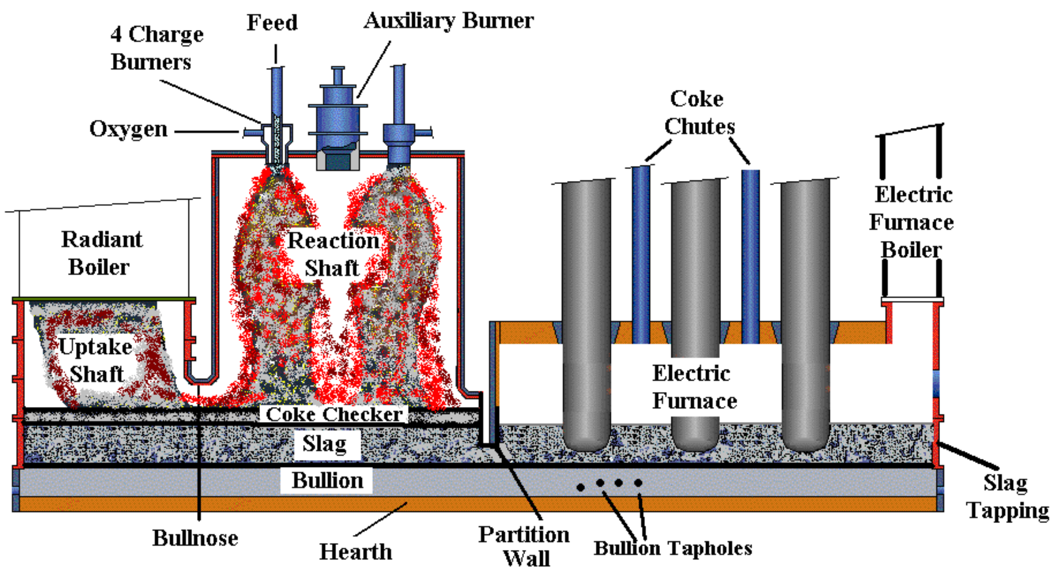

Figure 2 – Kivcet Furnace (3)

Concentrate burners at the top of the reaction shaft (4 at Cominco, 2 in Portovesme) serve to mix the pre-dried feed material with oxygen in order to spontaneously initiate the roasting and smelting reactions as the charge travels down the reaction shaft. The reaction shaft is made entirely of water-cooled copper tubes cast in copper elements from the centerline of the hearth. The reaction shaft is also equipped with a natural gas auxiliary burner (12,000 Mcal/h at Cominco) for heat during feed interruptions. The feed to oxygen weight ratio is crucial for the control of the desired reducing condition in the flame. An abundance of oxygen will increase the lead content in the slag and tend to form magnetite deposits under the reaction shaft whereas an oxygen deficiency will result in unburned feed and formation of a matte phase and sulfide deposits in the uptake shaft. Moreover, a rather erratic and varying feed composition is detrimental to the process making it extremely difficult to achieve stable operating conditions. Fluctuations in the fixed carbon content of the fuel coal should be minimized. The implementation of a residue blending device and storage bins for flue dust with loss-in-weight discharge are required to avoid poor blending of different residues and variations in the amount of recirculated flue dust (4).

At TeckCominco flame temperatures are monitored hourly under each concentrate burner at a predetermined distance from the burner and are used to adjust the feed calorific value. Flame temperatures lower than 1380°C are an indication that the charge is under-fueled and a coal increase is required in the charge. Flame temperatures over 1420°C indicate an excess of coal in the charge. As an additional measure the carbon content in the charge is to be analyzed frequently. Normal coal adjustments made for flame temperature control are 2.5-3.5% of the total coal in the feed material. Smelt samples taken under each burner are analyzed for sulfur. The goal for typical residual sulfur remaining in the smelt at 0.5-1.2% and are visually inspected for completeness of burn. A good smelt sample will be well fused. Poor smelt samples will be dusty, indicating unburned feed. Differences in smelt samples between burners can indicate a need to clean accretions from the burner tip. If not required otherwise, the burners are cleaned once per day.

Coarser coke (5-15 mm in size) enters the furnace together with the charge in order to float on the slag layer in the reaction shaft area forming a “coke checker”. The added coke rate is adjusted to maintain a coke layer of approximately 100-150 mm in thickness to efficiently reduce the generated lead oxide as the smelt flows through the coke. One control parameter of the coke layer thickness is maintaining the temperature of the coke checker between 1100-1200^{o}C. Coke checker temperatures higher than 1200^{o}C indicate a thin layer of coke in the furnace, temperatures below 1100^{o}C mean a thick layer of coke or coke piling, and the coke rate is increased or decreased, respectively. The coke checker condition is monitored hourly. In balance with the flame chemistry it is the most important factor to control the lead content in the slag (4). During times of poor coke checker performance, for example, the furnace would be operated with a more reducing flame to lower the lead content in the slag. This, however, can not be maintained indefinitely due to accretion formation against the sidewalls of the uptake shaft. These accretions mainly consist of lead sulfide and can eventually grow so large that they start blocking the gas passage at the “bullnose”. The bullnose accretion condition is monitored by measuring the draft differential between the reaction shaft and the boiler on a continuous basis. In order to reduce the bullnose accretion, the oxygen content to the burners is increased. When operating under flame reducing conditions, the operator must balance the lead oxide content in slag with the formation of bullnose accretion and challenged to accomplish an enhanced reduction from the coke checker. Accretion management and the directly dependent performance of the coke checker is one of the most critical control parameters to the entire operation and has a direct impact on the achieved furnace performance (4).

The molten and virtually reduced slag flows under a submerged water-cooled copper partition wall, which separates the electric furnace (55-m^2 at TeckCominco) from the reaction shaft. Three in-line electrodes deliver the required power (5-7 MW at TeckCominco) to complete the slag reduction, and to maintain the desired slag temperature between 1320-1360^{o}C. The majority of the zinc contained in the raw materials reports to the slag in the reaction shaft area. After entering the electric furnace compartment the zinc is volatilized depending on the adjusted reducing atmosphere and recovered as fume. Slag is discharged from the KIVCET furnace in regular intervals and can be granulated or transferred by means of water-cooled cast copper launders to a subsequent slag fuming furnace. At TeckCominco a normal slag tap lasts approximately 60-90 minutes consisting of about 80-95 t slag. Therefore, the slag depth varies in-between slag tapping intervals from 600 to 1000 mm. The furnace bullion level is maintained below 900 mm. The bullion is discharged at 850-950^{o}C through three specially designed 50-mm-diameter tapping inserts. Any matte layer generated in the furnace causes significant operational problems with bullion tapping. Its formation is minimized by controlling reaction shaft desulfurization and by tapping bullion at high temperatures to keep sulfides in solution. The bullion is transferred to a downstream refinery for further refining.

The hearth of the KIVCET furnace is constructed in the form of an inverted arch employing three different types of brick. Exposed to and in contact with the bullion is a 450 mm thick layer of magnesite-chrome bricks. To keep the potential risk of hydration of the magnesite-chrome bricks to a minimum, the last four perimeter bricks of the hearth are alumina-chrome bricks, as shown in Figure 3. The magnesite-chrome bricks rest on a 1 mm thin sheet of stainless steel. Below the stainless steel sheet is a layer of graphite bricks. This layer is 150 mm thick to uniformly distribute the heat from the hearth. At TeckCominco the hearth is air cooled through 14 channels below the graphite bricks, employing three variable-speed fans with a total capacity of 60 000 Nm^3/h. There are 8 thermocouples installed in the magnesite-chrome bricks to measure the temperature of the hearth. The hearth cooling fans are operated to maintain temperatures in the magnesite-chrome bricks between 300 to 350^{o}C minimizing penetration by liquid. The roof of the electric furnace is an arch design built entirely of magnesite-chrome brick. Thermal expansion of the hearth and the electric furnace roof is compensated by the installation of 52 springs in the hearth and 16 springs in the electric furnace roof. Due to different spring travel requirements, four different types of springs are applied in the furnace design. Each of them varies in size and spring tension. The spring compression was carefully set to 7 – 10 t on each spring before heat up. Spring movement is monitored every two days and has been 20 – 25 mm since start-up. Any movement of the spring measurements would be cause for concern and an investigation of the possible causes would be initiated (4).

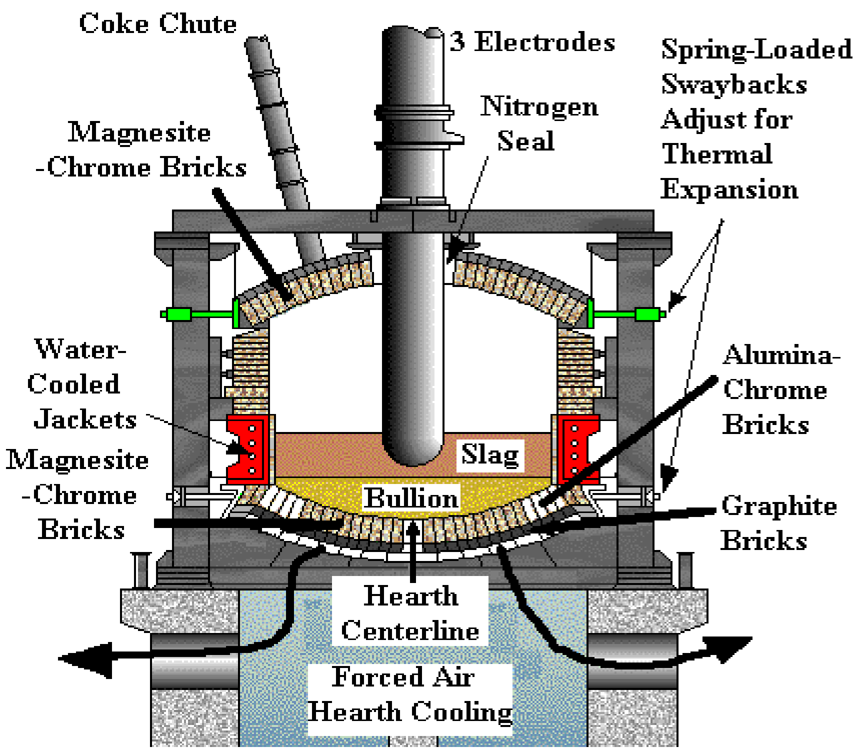

Figure 3 – Cross-section of Kivcet Electric Furnace (3)

The sidewalls of the KIVCET furnace are equipped with water-cooled copper jackets. The furnace at TeckCominco has a total of 207 independent cooling elements. A central distribution system with each discharge separated for independent metering is used to supply the cooling water. Three pumps, each rated at 1100 m^3/h at 3.5 Bar, are employed. Two pumps are running continuously and one pump is on standby. The inlet temperatures of the cooling water to the jackets are maintained at 40^oC with the typical outlet temperatures being 43-50^oC depending on jacket location. Two booster pumps are installed in the water supply line in order to increase pressure to 675 kPa for the existing lead bullion tapping jackets. The lead bullion tapping jackets are continuously monitored for jacket and water temperatures. A taphole is taken out of service as soon as the jacket and water temperatures indicate an abnormal elevation. Typically, each taphole insert will have a service life of about 200 taps but is exchanged at the first sign of deterioration (4).

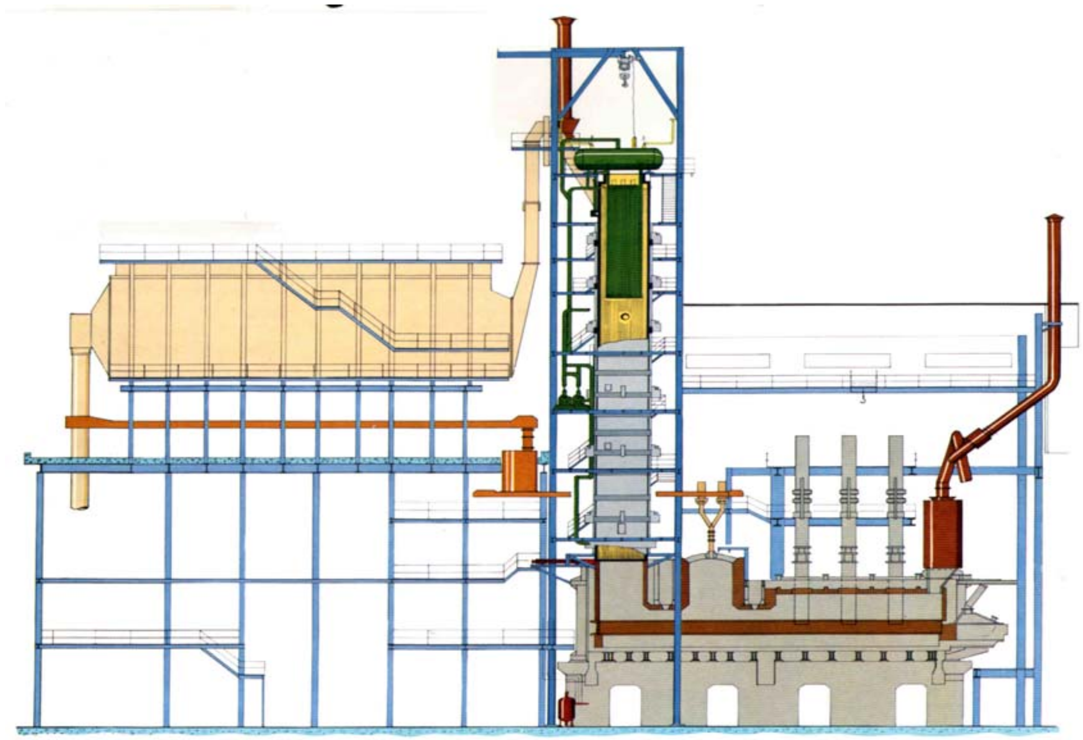

Figure 4 – Kivcet Waste Heat Boiler System at Portovesme

Compared to the conventional two-step process, the off-gas volumes are much smaller (21,000 Nm^3/h at TeckCominco; 12,000 Nm^3/h at Portovesme) and contain a much higher SO_2 concentration of 12% to 15%. This can be attributed to the application of nearly pure oxygen and the sealed design of the furnace. The off-gases enter a waste heat boiler system consisting of a radiant section, a downcomer section and a convective pass (Figure 4). The radiant section is a vertical uptake completely equipped with membrane walls cooling down the off-gas from 1375^0 C to maximum 830^0 C. In the downcomer section the off-gas is cooled further down to $600\text{-}630^0$ C before entering the convective pass containing heat tube bundles. The outlet gas temperature from the waste heat boiler is approximately 350^0 C. Typically, the boiler system produces steam (23-25 t/h at TeckCominco; 12-15 t/h at Portovesme). In case of the Portovesme plant, the thermal energy is converted in a turbine into electricity, which is utilized in the process minimizing outside energy requirements. The collected dust in the waste heat boiler is, together with the dust precipitated in the subsequent Hot-Gas ESP, recirculated back to the process.

The most recent available operating data of both Kivcet plants in operation are listed in the following table:

Kivcet Plants	**Portovesme srl Portovesme/Italy 1999**	**TeckCominco Trail/Canada 2001**
Lead Production in MTPY	100,000	85,000
Raw Material Consumption in MTPY	150,000	325,000
Ratio Primary : Secondary Materials	3.5:1	1:2
Type of Secondaries	Battery Paste, EAF-Dust, Zinc Oxide, Waelz Oxide	Recycled Battery, Zinc Plant Iron Residues, Pb Plant Drosses
Dryer Type	Rotary Drum	Rotary Drum
Feed Rate in MTPH	35	58
Inlet Moisture Content in %	8 – 10	13
Outlet Moisture Content in %	0.1	< 1.0
Off-Gas Volume in Nm^3/h	24,000	71,000
Kivcet Furnace Feed Rate in MTPD	600	1,220
Silica as Furnace Flux in Kg/T Bullion	92.8	170
Lime as Furnace Flux in Kg/T Bullion	154.4	480
Iron as Furnace Flux in Kg/T Bullion	23.2	540
Coal as Furnace Flux in Kg/T Bullion	-	440
Coke as Furnace Flux in Kg/T Bullion	50	110
Oxygen Volume in Nm^3/h	6,500	9,100
Air Volume in Nm^3/h (post-combustion)		1,500
Off-Gas Volume in Nm^3/h	12,000	22,000
SO_2 – Content in Off-Gas in %	22 – 25	~ 15
Steam from Waste Heat Boiler in MTPD	300 – 350	670
Bullion Production in MTPD	300	260
Matte Production in MTPD	10	13
Slag Production in MTPD	120	590
Pb in Slag in %	4	5.9
FeO Content in Slag in %	26	27.9
SiO_2 Content in Slag in %	22	21.6
CaO Content in Slag in %	20	13.3
Zn Content in Slag in %	9	18

Table 1 – Main Operating Parameter of the Kivcet Plants

QSL Technology

The QSL-technology is a continuous operating bath smelting process. The process principles of treating metal sulfide concentrates in one smelting unit were developed and patented by two Americans, Prof. Paul E. Queneau and Prof. Reinhardt Schuhmann. Based on the patent the German companies Lurgi AG and Berzelius Metall GmbH developed the QSL-process for the recovery of lead to an industrial scale after operating a semi-commercial plant for several years. Today, two plants based on the QSL technology are in operation, one at Korea Zinc in Onsan/South Korea with a production rate of 130,000 tpy of lead and at Berzelius Metall GmbH in Stolberg/Germany with an annual lead production of about 110,000 t.

The entire converting process is incorporated in one single, slightly inclined (0.5%), closed, kiln-like smelting unit. The converter is divided by a partition zone into a smelting and a slag reduction zone (Figure 5). It can be tilted by 90^0 about its longitudinal axis when the process is interrupted. The process is designed to treat all grades of lead concentrates as well as secondary materials, applying the bath smelting principle with submerged high-pressure injection of tonnage oxygen and fossil fuels. Depending on the desired material composition to be treated and the overall lead production, generally two different converter sizes are applied. The QSL-converter at Korea Zinc has a diameter of 4/4.5 m and an overall length of 41m and is designed to treat higher amounts of secondary materials. The converter at Berzelius has a diameter of 3/3.5 m and a length of 33 m and treats larger volumes of primary materials. The current ratio of primary to secondary material at the smelter in Onsan is 2:1 and in Stolberg 2.75:1. Both operations, however, report a high flexibility of the process in terms of feed composition. They can deal with a wide variety of feed materials and quickly adapt to changes in the feed composition. Rates of secondary materials of more than 60% have been charged already in the past on a monthly basis.

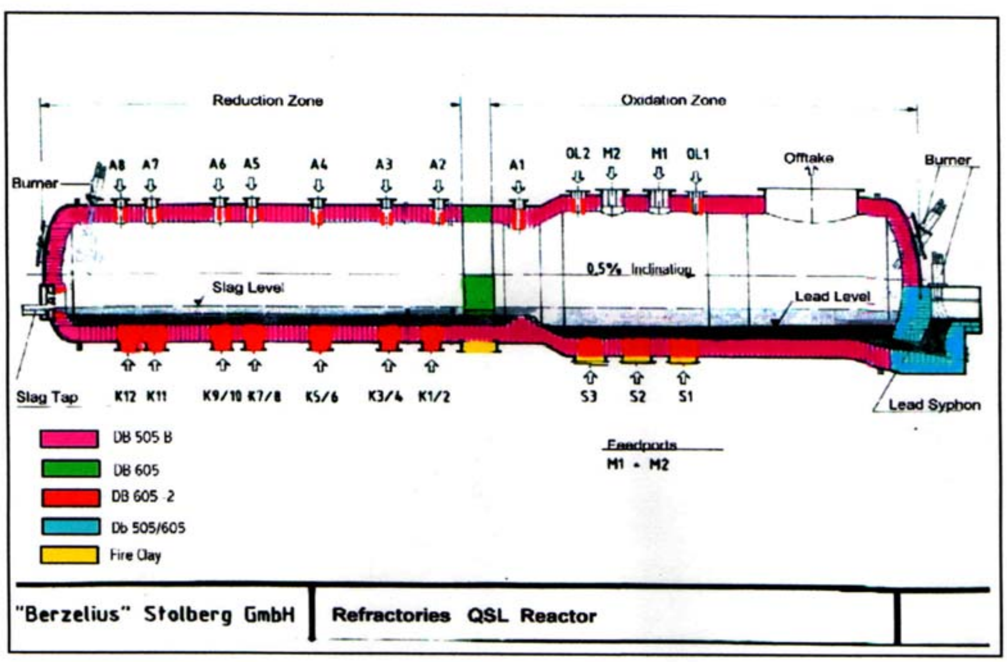

Figure 5 – QSL-Converter at Berzelius Stolberg GmbH (5)

The converter is equipped with high-quality chrome-magnesite refractory lining. In areas, which are exposed to more severe conditions causing potentially higher rates of refractory wear such as the partition wall and the bricks adjacent to the submerged injectors, superior chrome-magnesite refractory qualities are applied. Overall, a service life of the refractory lining between 1 to 2 years has been achieved without applying water-cooling elements.

The feed preparation is relatively simple consisting only of bins for material storage, weighing devices for composing the anticipated charge mixture and a mixer in order to thoroughly blend and agglomerate the charge to satisfy steady-state feed requirements. Lead scrap materials can be directly charged into the converter. The moist and agglomerated feed mixture is then charged homogeneously and weight controlled through feed ports located in the roof of the smelting compartment into the converter. It falls into a dispersed molten mixture consisting of “primary” slag and crude lead while oxygen is injected through submerged gas/water aerosol-cooled tuyeres at the bottom of the converter. In the liquid bath an autogenous roast reaction smelting is initiated converting some of the lead compounds directly into low-sulfur lead bullion and forming a “primary” slag with a lead oxide content of 35-45%. For better process control, the lead content in the slag is measured every 1 – 2 hours by taking a sample through a sample port and the oxygen to feed ratio is adjusted correspondingly, if required. The exothermic reaction takes place at 1050 – 1100^0 C and is monitored with permanently installed thermocouples as well as manual temperature measurements with disposable thermocouples. The oxidizing atmosphere can be controlled by increasing or decreasing the amount of charged fuel or the oxygen to feed ratio. As fuel, low cost available materials like bituminous coal or petroleum coke can be applied. During feed interruptions heat is provided by injecting natural gas through the tuyeres and combusting it in the converter with an air/oxygen mixture.

The slag flows through a submerged opening in the partition wall into the slag reduction zone where the lead oxide is gradually reduced to metallic lead using pulverized coal as the reducing agent while the slag flows to the opposite end of the converter. The coal is injected with a carrier medium into the melt through a series of bottom blowing gas-cooled tuyeres together with a controlled amount of supplementary oxygen to adjust the desired reduction potential in the melt. Reduction is effected by arranging the injectors for the carbothermic reduction providing a continuous mixer settler regime. In addition, the oxygen activity is progressively decreased over the entire length of the reduction zone and slag temperature steadily increased before slag discharge. The independently and accurately controlled gas analysis injectors are spaced sufficiently apart to form, at minimal splashing, a series of properly reaction gas-slag bubble plumes of sequentially decreasing oxygen activity and increasing temperature until slag is discharged. These chemically active mixing areas are separated by passive lead settling zones. There is virtually no interaction of adjacent bubble plumes, thus creating a continuous mixer-settler configuration (6). At the end of the slag reduction zone a larger settling area is provided in order to accomplish sufficient separation between the low-lead slag and the lead. This region may be heated by means of an auxiliary oxy-fuel burner, which is installed in the roof of the converter. The settled metallic lead flows countercurrently to the slag back into the smelting zones. It combines with the primarily produced lead bullion before being tapped through a siphon system for subsequent conventional refining. The final slag is tapped at the end of the slag reduction zone and granulated. The carbothermic reaction is endothermic and takes place at 1150^0 – 1250^0 C. Required postcombustion, mainly of the gases in the slag reduction is accomplished with oxygen-enriched air, which is injected into the gas atmosphere via lances. These lances are located in the roof of the converter over its entire length.

The QSL-process applies nearly pure oxygen, which contributes, like the Kivcet-technology, to a comparatively small volume of highly SO_2-rich off-gas. The actual off-gas volume for the plant in Stolberg is 23,500 Nm^3/h with more than 14% SO_2 depending on the type of concentrates. For the Korea Zinc plant to off-gas volume accounts to approximately 35,000 Nm^3/h with SO_2-concentration between 10% and 15%. While in the converter in Stolberg the off-gas from the reduction zone is combined with the generated off-gas in the smelting zone through an opening for the passage of the process gas, the converter at Korea Zinc has a completely closed partition wall separating the off-gases from both zones. Depending on the adjusted gas atmosphere in the slag reduction zone the resulting process gas contains zinc fumes. The gas exits the converter through a second uptake and the fumes are collected for subsequent zinc recovery. This lowers the cost of the slag fuming operation carried out in a separate furnace. The produced slags contain 5% lead on average in the Korea Zinc plant and 3% to 4% lead in Stolberg. It was demonstrated already that discharge slag of well less than 2% are obtainable, but only when zinc is simultaneously fumed at strong reduction potentials. In Stolberg the zinc is then collected in the flue dust. This is undesirable because the flue dust is being directly recirculated to the converter and it would contribute to a substantial proportion of total feed by weight. Slags containing more than 15% zinc are generally too viscous at adjusted converter temperature. Heat is recovered from the off-gas in both plants and utilized in order to minimize outside energy requirements. In general, the off-gases are cooled in a waste heat boiler system consisting of a vertical radiation channel and a subsequent convective pass. In the vertical uptake the gases are cooled to a temperature below 700^0 C. The exiting temperature of the off-gas after the convective pass is between 350^0 C and 380^0 C. In the subsequent hot-gas electrostatic precipitator the off-gas is dedusted to a content less than 100 mg/Nm^3. Collected dust is immediately recirculated back to the process. After passing the SO_2-rich off-gas through several gas-cleaning stages it enters a double catalysis sulfuric acid plant to produce sulfuric acid at conversion rates of 99.5%.

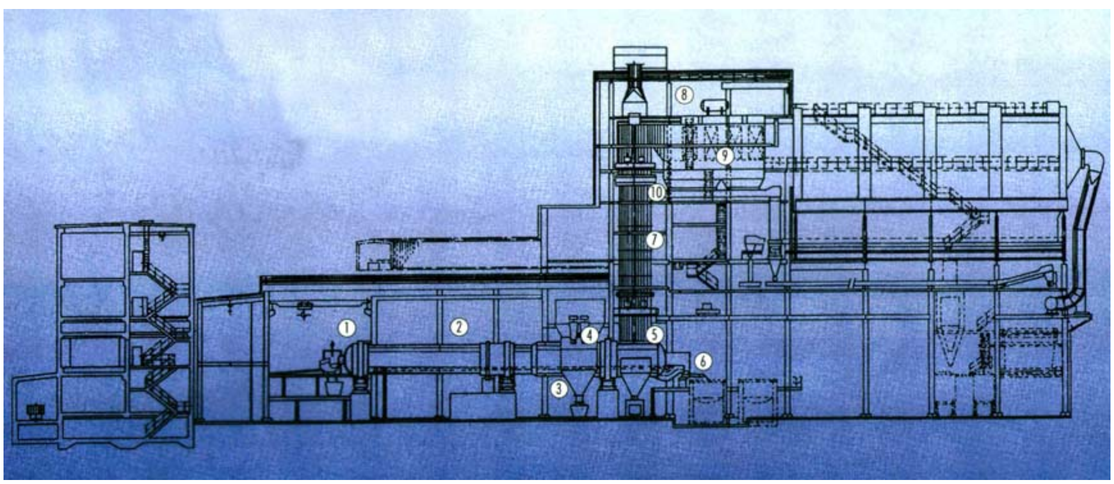

Figure 6 – QSL-Plant at Berzelius Stolberg GmbH

1. Slag Tap QSL Converter; 2. QSL Converter; 3. Location of Three Oxygen Injectors; 4. Reactor Charging; 5. Off-gas Opening; Transition Converter/Waste Heat Boiler; 6. Lead Siphon with Decopperizing Kettle; 7. Radiation Channel of Waste Heat Boiler System; 8. Steam Drum of Waste Heat Boiler System; 9. Convection Pass of Waste Heat Boiler System; 10. Chain Conveyor System for Flue Dust Recirculation

Since the commissioning of the first commercial QSL-plant in 1990, the gained operating experience has led to a number of modifications to the converter and preceding or subsequent equipment which were implemented during a number of plant shut downs in Stolberg (7, 8).

Several of these modifications were already incorporated in the Korean plant design, and additional improvements were also implemented (7). The current main operating data of both QSL-facilities are summarized in the following table:

QSL Plants	**Berzelius Metall GmbH Stolberg/Germany 2001**	**Korea Zinc Onsan/Korea 2001**
Lead Production in MTPY	105,600	130,000
Raw Material Consumption in MTPY	176,000	314,000 (WMT)
Ratio Primary : Secondary Materials	2.75:1	2:1
Type of Secondaries	Battery Paste, Zinc Plant Residues, Slags, Scrap	Pb-Residues, Pb-Ag Residues, Battery Paste
QSL Furnace Feed Rate in MTPD	612	1,500 – 1,600
Inlet Moisture Content in %	8 – 10	10 – 12
Silica as Furnace Flux in Kg/T Bullion	74	20
Lime as Furnace Flux in Kg/T Bullion	230	117
Iron as Furnace Flux in Kg/T Bullion	150	148
Coke as Furnace Flux in Kg/T Bullion	23	-
Coal in Kg/T Bullion	115	131
Oxygen Volume in Nm^3/h	3,570	9,400 – 9,900
Air in Nm^3/h	200	1,500
Oxygen Enrichment in Air in %	67	-
Off-Gas Volume in Nm^3/h	23,500	33,000 – 38,000
SO_2 – Content in Off-Gas in %	14.1	10 – 15
Steam from Waste Heat Boiler in MTPD	300	480
Bullion Production in MTPD	370	440
Matte Production in MTPD	16.5	-
Slag Production in MTPD	274	300
Pb in Slag in %	3 – 4	4 – 6
FeO Content in Slag in %	29.2	27 – 29
SiO_2 Content in Slag in %	20	20 – 22
CaO Content in Slag in %	20.8	14 – 15
Zn Content in Slag in %	8.8	15 – 16

Table 2 – Main Operating Parameter of the QSL-Plants in 2001

Ausmelt Technology

The Ausmelt technology is derived from the Sirosmelt top submerged lance process. That technology has been developed over the past twenty years in laboratory and pilot plant scale studies on the recovery of almost the complete range of non-ferrous, ferrous and precious metal materials and is successfully applied in the copper, nickel, silver, tin and zinc industry. The initial design for lead smelting consisted of a two furnace arrangement. For lead smelting two furnaces are commercially in operation. Metaleurop Weser Blei in Nordenham, Germany commissioned a smelter in 1996 with the intention to perform the two stage operation for lead recovery in one single furnace. The smelter has a design production rate of 90,000 tpy of lead based on a certain ratio of primary to secondary raw materials. Korea Zinc contracted with Ausmelt for the second lead smelter. It was commissioned in 2000 and processes lead oxide fume, sulfate residue and battery paste (9).

The process concept and the principles of the furnace design are illustrated in Figure 7.

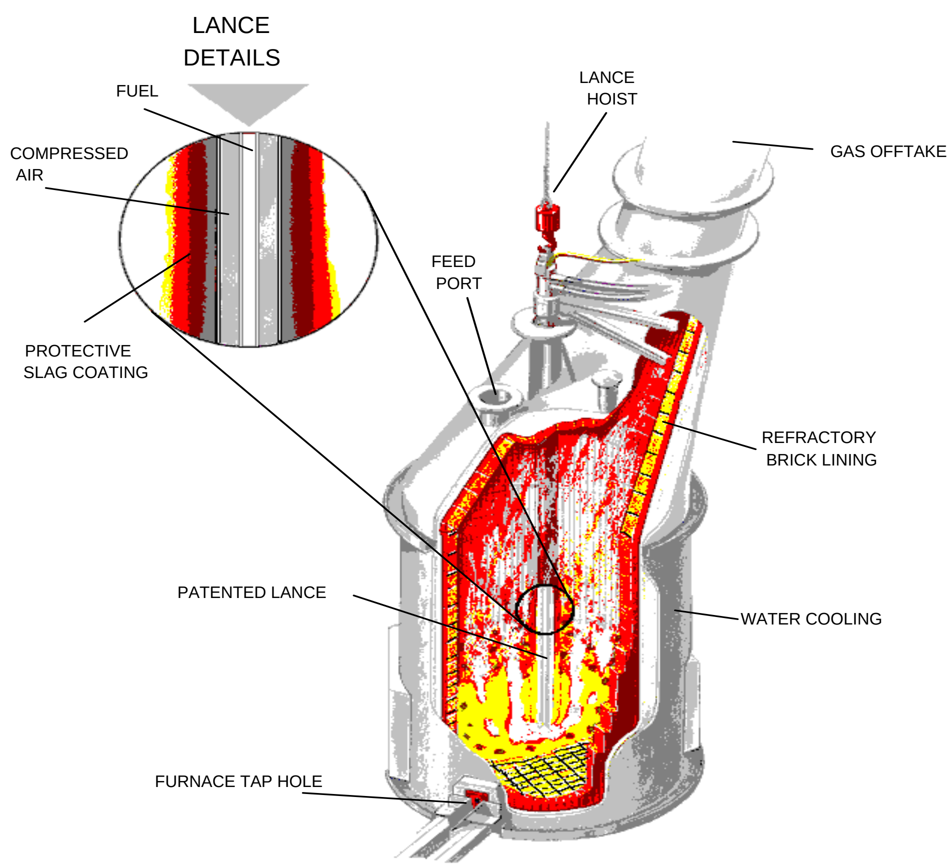

Figure 7 – A Schematic Section through an Ausmelt Furnace

Raw materials and additives are stored in bins from where a feed delivery and weigh control system collects and composes the desired charge composition and transports it to a mixing device for blending and homogenizing before being fed into the furnace. Like in the QSL technology the materials do not have to be dried or reduced to a specified material size before charging. The coarse, moist and agglomerated charge is dropped through a feed port located in the inclined roof hood of the furnace and incorporated into the melt. Required air, process fuel and fine materials are injected beneath the surface of a liquid slag bath through a top entry submerged lance system. Oxygen enriched air to levels up to 50% may be used with the specially designed lance, injecting the gas through the outer annulus while the fuel and the fine materials are conveyed down the lance through an inner tube. The stainless steel lance is protected from the furnace contents by a coating of frozen slag in order to minimize lance wear. The coating is established by carefully lowering the lance into the furnace with an intermitted stop above the bath permitting slag to splash and freeze on the lance before submerging the tip of the lance. During operation, the latter is always below the theoretical static slag line. The media are therefore injected into the slag creating very turbulent conditions in the furnace promoting very rapid reactions resulting in high smelting capacities at small areas.

The furnace is usually constructed as a refractory-lined cylinder applying a high-quality chrome-magnesite refractory lining. Where very aggressive slags, mattes or metals are present or higher temperatures are employed, water cooling is applied behind the bricks to ensure acceptable refractory life. Operating experience, nevertheless, has shown that the turbulent conditions create extreme working atmosphere for the refractories and may result in relatively high wear rates.

A slag reduction process to produce bullion and discard slag follows the oxidation smelting process step. Precise control of the system oxidation state is a key feature of Ausmelt lance technology. This, together with the addition of a reductant, such as coal, allows the reduction step to be precisely tailored to meet specific requirements. A low oxygen potential in the order of 10^{-9} to 10^{-10} atmosphere is maintained The liquidus temperature of lead oxide containing slags is raised from 1000°C to 1100°C to 1150°C to 1250°C as the lead in slag drops from more than 40% Pb to about 10% Pb. Fluxing with limestone may be needed in order to substitute lead oxide by calcium oxide and to prevent the precipitation of zinc ferrite or magnetite from zinc and iron rich slags with lead levels in the region 15 - 40% Pb in the temperature region of 1200°C. Slag reduction is a less economic exercise than smelting of high lead content material directly to bullion, particularly with solid slag processed on a campaign basis. Lead oxide fume is produced in increasing quantities with increasing temperature, collected in a baghouse or ESP and recycled to the smelting furnace, with or without external fume treatment for impurity removal.

In both stages, smelting and reduction, air is introduced into the top space of the furnace through a shroud pipe attachment on the Ausmelt lance to post-combust any volatilized species. Up to 40% of the energy generated by these reactions is recovered for utilization in the bath (10).

The overall process concept can consist of either single, batch, two furnace continuous, two furnace continuous and batch, or three furnace continuous process option(s). Ausmelt’s preferred approach for the two stage operation of lead smelting is to use two furnaces where slag flows continuously from the smelting to the reduction furnace via weirs, siphons and launders. A process block diagram of this alternative is shown in Figure 8 (9). In general, the second furnace is smaller than the primary furnace, particularly when smelting high grade feed. Even though the second furnace is smaller, it requires a separate gas handling system typically incorporating an evaporative gas cooler and baghouse, and this increases plant capital cost above that of the single furnace, two stage operation. The final slag product from the second furnace typically contains low levels of lead but may well contain appreciable levels of zinc (8-12% Zn). The slag can be granulated and held for long term storage or a second slag reduction can be carried out to recover the zinc as a high grade (>50% Zn) fume, as previously described and produce a discard slag containing low levels of lead (<1% Pb) and zinc (<3% Zn).

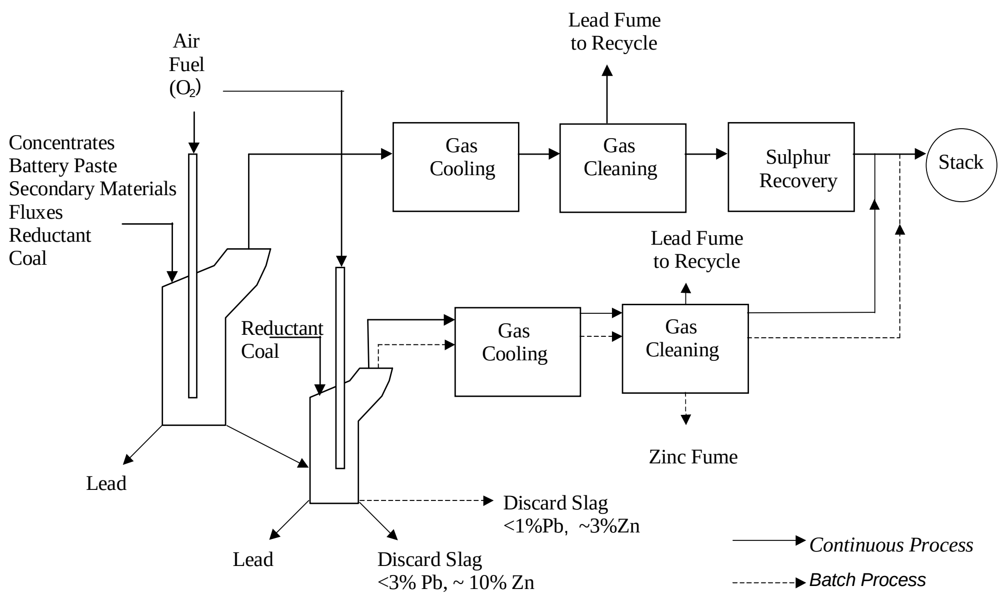

Figure 8 - Two Furnace Continuous Process with no Zinc Recovery or Two Furnace Continuous/Batch with Zinc Recovery

The two furnace process option has not yet been employed for lead smelting. Metaleurop in Nordenham, Germany opted for the single furnace route. Originally designed for a batchwise operation consisting of smelting lead-rich primary and secondary raw materials and the reduction of the generated lead oxide rich (50 – 60%) slag in campaigns, it is performing only oxidized smelting of lead bearing materials due to economical reasons. Commencing operation in March 1996, the smelter experienced initial mechanical as well as process oriented problems mainly with respect to insufficient service life of the refractories, the performance of the incorporated circulating fluidized bed boiler for waste heat recovery and obtaining the anticipated slag reduction rates in terms of lead content and its impact on the overall economical operation. After addressing these problems and carrying out several modifications to the entire process design, the plant is now achieving the production results envisaged at the project commencement, as reported by Metaleurop (11). The plant processes a variety of feed materials including primary and secondary lead bearing materials. The current main operating data of the Ausmelt facility in Nordenham are summarized in the following table:

Ausmelt Plant	**Metaleurop Nordenham, Germany 2001**
Lead Production in MTPY	125,000
Raw Material Consumption in MTPY	190,400
Ratio Primary : Secondary Materials	1:2
Type of Secondaries	Battery Paste, Residues, Scrap
Furnace Feed Rate in MTPD	670
Silica as Furnace Flux in Kg/T Bullion	300 – 600
Lime as Furnace Flux in Kg/T Bullion	500 – 1,300
Iron as Furnace Flux in Kg/T Bullion	500 – 1,000
Coal as Furnace Flux in Kg/T Bullion	-
Coke as Furnace Flux in Kg/T Bullion	1,000 – 3,000
Oxygen Volume in Nm^3/h	1,600
Air Volume in Nm^3/h	7,000
Oxygen Enrichment in Air in %	30 – 40
Off-Gas Volume in Nm^3/h	30,000
SO_2 – Content in Off-Gas in %	6 – 7
Steam from Waste Heat Boiler in MTPD	340
Bullion Production in MTPY	139,000
Matte Production in MTPY	5,800
Slag Production in MTPY	46,000
Pb in Slag in %	50
FeO Content in Slag in %	11 – 12
SiO_2 Content in Slag in %	5 – 7
CaO Content in Slag in %	2 – 3
Zn Content in Slag in %	6 – 10

Table 3 – Main Operating Parameter of the Ausmelt Furnace at Nordenham in 2001

Kaldo Technology

Boliden Metall AB developed the Kaldo process and the operation in Rönnskär/Sweden is the sole application in the lead industry. The plant is used not only for lead smelting but also for the treatment of secondary raw materials containing copper, precious metals and plastics. The process is based on the flash smelting principle and operates on a discontinuous / batchwise basis and consists of a top blowing rotary converter. It has special features compared to the other processes. The batchwise operating mode seems to make the process not well suitable for large-scale operation but the furnace is a very flexible unit and can treat a wide range of secondary materials including battery scrap, residues and recycled dust amongst lead concentrates. It was exclusively using concentrates from its own Laisvall mine as lead bearing raw material but recently has to treat other concentrates. Like in other flash smelting applications the feed material has to be dried to moisture contents less than 1% before being blown through a lance into the furnace, where it reacts in the flash with the oxygen-enriched air that is introduced. Iron and lime fluxes are also added in order to bind the silica in the concentrate generating a liquid slag. The generated slag contains high concentrations of lead oxide, which is reduced to average lead contents of approximately 4% by coke. The lead bullion and the slag are then discharged into separate ladles. The lead is subsequently treated in a refinery, while the slag is returned to a mine for final underground disposal. The converter is completely encapsulated in a vented enclosure generating off-gas volumes of 25,000 Nm^3/h with SO_2-concentration between 4% and 5%. The off-gases are combined with process gas from the adjacent copper smelter to produce sulfuric acid.

Kaldo Plant	**Boliden AB Metal Rönnskär/Sweden 1999**
Lead Production in MTPY	35,000
Raw Material Consumption in MTPY	43,000
Ratio Primary : Secondary Materials	100:0
Dryer Type	Rotary Drum
Feed Rate in MTPH	30
Inlet Moisture Content in %	5
Outlet Moisture Content in %	<0.1
Off-Gas Volume in Nm^3/h	15,000 – 20,000
Furnace Feed Rate in MTPD	Batchwise
Silica as Furnace Flux in Kg/T Bullion	-
Lime as Furnace Flux in Kg/T Bullion	203
Iron as Furnace Flux in Kg/T Bullion	217
Coal as Furnace Flux in Kg/T Bullion	-
Coke as Furnace Flux in Kg/T Bullion	48
Oxygen Volume in Nm^3/h	Enrichment
Off-Gas Volume in Nm^3/h	25,000
SO_2 – Content in Off-Gas in %	4 – 5
Bullion Production in MTPD	Batchwise
Slag Production in MTPD	Batchwise
Pb in Slag in %	4.2
FeO Content in Slag in %	40
SiO_2 Content in Slag in %	21
CaO Content in Slag in %	28
Zn Content in Slag in %	4.6

Table 4 – Main Operating Parameter of the Kaldo Plant in 1999

Conclusion

The lead industry is indeed economical and technological at a crossroad. With the introduction of new lead smelting technologies during the last decade an exciting period started during which a revolution will be made in lead smelting and the traditional smelting processes will yield to new pyrometallurgical technologies. Environmental pressures have strongly influenced many of the most significant and recent developments in the lead industry, either directly or indirectly. It is inevitable that environmental concerns will remain at the top of the agenda. With the majority of lead used in batteries close to 85% of all lead bearing products are recyclable. One direct consequence is the steadily increasing recycling rate of lead bearing scrap. It is probable that most, if not all, growth in lead demand can be met without increasing mine production. This requires that the lead smelters must accommodate more and more secondary materials in their feed material. The traditional sinter machine / blast furnace operation is not only challenged by direct smelting processes but after overcoming initial problems these new technologies are now more than major competitors. It seems that the Kivcet- and the QSL-processes are well established and mature technologies introducing a new era of lead smelting. They are economically and particularly environmentally viable technologies and offer several advantages. The Ausmelt- or the similar Isamelt-technology as well as the Kaldo furnace offer additional alternatives for economical lead smelting complying with the increasingly stringent environmental regulations. The ongoing introduction of more stringent regulation of pollution control in many countries will be most likely the prime motive for further modernization in the future.

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